

# FOOD PRODUCTS AND DIETARY SUPPLEMENTS CONTAINING PHENOLATED PROTEINS AND PROCESS FOR PREPARING THE SAME

## BACKGROUND OF THE INVENTION

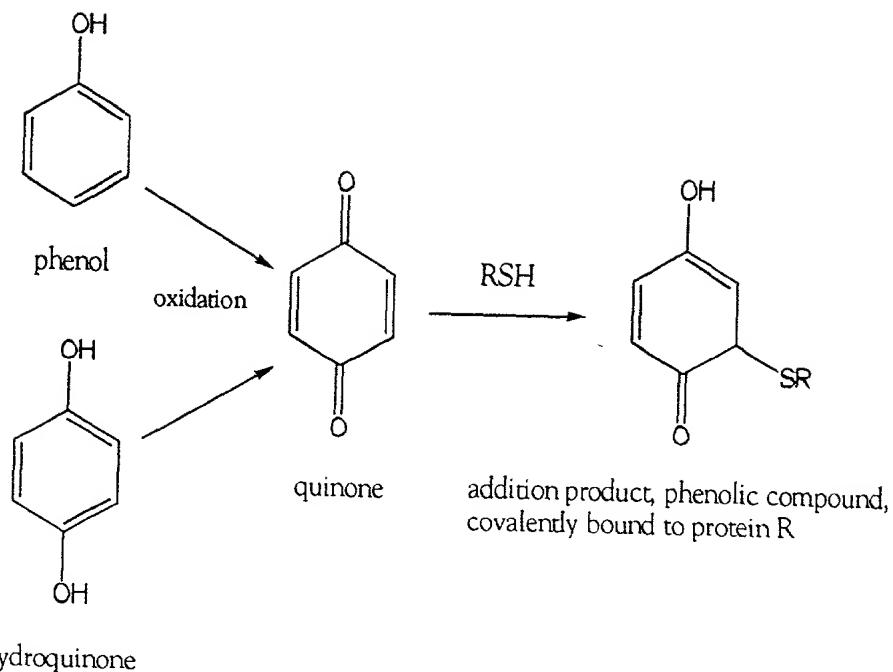
## Field of the Invention

The present invention is in the field of dietary supplements and foods. More particularly, the present invention relates to dietary supplements and food products containing phenolated protein substances having anti-oxidant properties, and to the process of manufacturing such dietary supplements and food products from vegetable sources for oral consumption by humans.

## Brief Description of Background Art

It has been known for a long time that many plant materials contain phenols or phenolic compounds. The term phenols, phenolic compounds or plant phenolics in the context of plant materials and in the context of the present application for patent refer to a multitude of naturally occurring substances which have one or more phenolic hydroxyl groups. As is known, a phenolic hydroxyl group is a hydroxyl group (OH) attached to a carbocyclic aromatic ring. Phenol (hydroxybenzene) is the simplest example of a phenolic compound, but the naturally occurring phenols or phenolic compounds tend to be of more complex structure, and include polyphenols having complex substitution patterns and compounds having condensed rings. Phenolics isolated from plants including seeds and fruits of plants include gallic acid, flavan-3-ols, flavonols, phloridzin, cinnamates, hydroxymethyl furfural and anthocyanins.

1 Phenolics compounds contained in plant materials, particularly in plant materials  
2 from which proteins are isolated for human or animal consumption, have long been  
3 considered undesirable. This is primarily because phenolics tend to bind strongly to  
4 proteins (by hydrogen bonds) and also by covalent bonds, and tend to provide undesired  
5 color to the plant protein isolates. Whereas the present applicant does not wish to be  
6 bound by theory, it is noted that the process by which phenolic compounds are bound to  
7 proteins is generally understood to involve a step of oxidation that occurs while the plant  
8 isolate is in aqueous suspension or solution, and is exposed to atmospheric oxygen, or to  
9 oxygen dissolved in water, followed by a 1,4 addition (Michael addition) of a sulphydryl  
10 (SH) or amino (NH) function of the protein to the resulting quinone. This series of  
11 reactions is illustrated below in a simplified form. The reaction below is simplified,  
12 because the plant phenolic compound is not simple phenol or hydroquinonone as  
13 illustrated below, but a more complex phenolic compound of the nature described above.  
14 The group **R** in the simplified scheme represents the rest of the plant protein molecule,  
15 just like the simple phenol or hydroquinone in the simplified scheme represents the more  
16 complex phenolic compound naturally occurring in the plant.



A detailed description and review of the chemistry of the attachment of plant

phenolics to plant proteins by hydrogen bonding and through oxidation to quinones

followed by 1,4 (Michael) addition, can be found in the publication by *Loomis et al.*,

“Plant phenolic compounds and the isolation of plant enzymes” *Phytochemistry*, **5**, 423,

(1966).

Because the plant phenolics are generally considered in the prior art to be

undesirable contaminants of proteins which are isolated from the plant, the prior art has

strived to isolate the proteins free of the phenolics, and to discard the undesirable

phenolics while keeping the desired protein material. Thus, processes for removing the

1 phenolics from plant proteins, and to isolate proteins as free of phenolic contaminants as  
2 possible, are described in several publications and patents, such as:

3 *Lusas* “Sunflower Seed Protein”, New Protein Foods, **5**, 393-433, (1985);

4 *Sodini et al.* J. Agric. Food Chem., **25**, 822-825, (1977), and

5 *Pearce* United States Patent No. 4,435,319.

6 Perhaps because of the difficulty or expense of removing “undesirable” phenolics

7 from phenolics-rich plant flours, the phenol-rich flours are typically considered to be of  
8 poor quality for human or animal consumption and are hence abundant and inexpensive.

9 These typically are by-products of oil extraction (e.g., flax meal) or represent a by-  
10 product of a specialized milling fraction (e.g., buckwheat).

11 In addition to being considered undesirable as a colorant, plant phenolics were also  
12 suggested to have anti-nutritive value (Food Phenolics, Chapter 6, p. 171-9, 1995).

13 On the other hand, it has been relatively recently recognized in the prior art that  
14 oral consumption of antioxidants increases serum antioxidant levels (see *Rao et al.*, J.  
15 Medicinal Food, **3**, 15, 2000) and that orally consumed anti-oxidants have beneficial  
16 value to human (and other mammalian) health. More specifically, the health benefits or  
17 potential benefits shown by epidemiological studies and generally attributed to  
18 consumption of anti-oxidant rich food or food supplements include or relate to prevention  
19 of various cancers, decrease in the incidence of cardiovascular disease, and decrease in  
20 the incidence of stroke. Recognizing the importance of anti-oxidants in foods or food

1 supplements, the prior art has actually developed an assay for determining the amount of  
2 anti-oxidants contained in a food product. The assay termed the Oxygen Radical  
3 Absorbance Capacity Assay (ORAC) is described by *Cao et al.*, in Clinical Chemistry,  
4 **41**, 1738, 1995. This assay allows one to quickly compare the total antioxidant capacity  
5 of various food servings (*Prior et al.* J. Amer. Nutraceutical Assoc., **2**, 46, (1999)).

6 As an exception to the prior art generally making great efforts to remove  
7 undesirable phenolics from isolated plant proteins, buckwheat protein from which  
8 phenolics have not been removed has been reportedly fed to experimental rats, as is  
9 described in a series of publications:

10 *Kayashita et al.*, Nutrition Research, **15**, 691-8, 1995;  
11 *Kayashita et al.*, J. Nutrition **127**, 1395, 1997;  
12 *Kayashita et al.*, Biosci. Biotechnol. Biochem., **60**, 1530, 1996;  
13 *Kayashita et al.*, Current Advances in Buckwheat Research, 935, 1995;  
14 *Kayashita et al.*, BioSci. Biotechnol. Biochem., **63**, 1242, 1999, and  
15 *Kayashita et al.*, BioSci. Biotechnol. Biochem., **63**, 1837, 1999.

16 In these publications about buckwheat protein, the authors suggest that whatever  
17 health effects were observed in the experimental rats they were entirely due to the protein  
18 composition of the buckwheat *versus* soy protein or casein. The authors discuss in detail  
19 the amino acid profiles of buckwheat protein and find several features of buckwheat  
20 protein that suggest health benefits. Indeed, buckwheat has been shown in the prior art to

1 have great health benefits independent of its protein or phenol content. Hence, any  
2 phenolic compounds which may have been present in the buckwheat protein of these  
3 experiments would have been considered impurities, and thus feeding of protein-phenol  
4 complexes to animals is not suggested by these publications of *Kayashita et al.*

5 **SUMMARY OF THE INVENTION**

6 It is an object of the present invention to provide a food supplement, food product  
7 or nutraceutical which is rich in vegetable protein bound plant phenolics having anti-  
8 oxidant properties.

9 It is another object of the present invention to provide a food supplement, food  
10 product or nutraceutical which is rich in vegetable protein bound plant phenolics having  
11 anti-oxidant properties and which utilizes readily available relatively inexpensive plant  
12 sources for the manufacture of such products.

13 It is still another object of the present invention to provide a process for the  
14 manufacturing of food supplements, food products or nutraceuticals which are rich in  
15 vegetable protein bound plant phenolics having anti-oxidant properties.

16 These and other objects and advantages are attained in accordance with one aspect  
17 of the invention by isolating protein material from vegetable sources of the type which is  
18 known to contain relatively high concentration of plant phenolics, such as buckwheat,  
19 sunflower seeds, soy beans, hops, mustard seeds, cottonseeds, peanuts, safflower seeds,  
20 rapeseed, flax seeds, by dissolving or suspending flour from said vegetable source in  
21 water, adding base to make the aqueous solution alkaline in a pH range of approximately

1 8 to 13, allowing oxidation of phenolic materials to occur by exposure to air or to oxygen  
2 dissolved in the water, acidifying the solution to a pH in the range of 2 to 7 by addition of  
3 acid, isolating the precipitated solids containing plant phenolics covalently bound to  
4 proteins, and incorporating said isolated plant phenolics covalently bound to proteins in  
5 foods, food supplements and in nutraceutical products.

6 In accordance with another aspect of the present invention exogenous phenolic  
7 products, such as phenolic acids (caffeic acid, gallic acid), catechins (epicatechin,  
8 catechin, gallicatechin gallate, epigallicatechin gallate), flavones (quercetin, myricetin,  
9 kaempferol), anthocyanidins (cyanidin, delphinidin, malvidin), or isoflavones (diadzein,  
10 genistein) are added to the vegetable flour dissolved or suspended in water, before it is  
11 rendered alkaline or while it is alkaline, so that the exogenous phenolics also bind  
12 covalently to the vegetable protein. Thereafter, the phenolics bound to the protein is  
13 isolated and utilized in the above-described manner. The isolated vegetable protein bound  
14 phenolics containing phenolics from the natural source and the added phenolics as well,  
15 are also incorporated in foods, food supplements and nutraceutical products.

16 The foods, food supplements and nutraceutical products of the invention have high  
17 antioxidant capacity as measured by the aforesaid Oxygen Radical Absorbance Capacity  
18 Assay (ORAC) test. The products of the invention having vegetable protein bound  
19 phenolics include, drinks such as shakes, bars, capsules, tablets, soft-gel capsules and  
20 other conventional forms in which foods, food and dietary supplements and nutraceuticals  
21 are provided for human consumption.

## DETAILED DESCRIPTION OF THE INVENTION

2 Vegetable protein bound phenolics can be obtained in accordance with the present  
3 invention from all such vegetable sources which usually serve as sources for vegetable  
4 proteins, for example buckwheat, sunflower seeds, soy beans, hops, mustard seeds,  
5 cottonseeds, peanuts, safflower seeds, rapeseed and flax seeds. The flour from these  
6 vegetable sources usually contains naturally occurring phenolics. As noted in the  
7 introductory section, the prior art has usually strived to separate the phenolics from the  
8 vegetable protein and discard it. In accordance with the present invention these naturally  
9 occurring phenolics are allowed to bind covalently to the protein.

10 Flour of the vegetable, such as of the above-noted buckwheat, sunflower seeds,  
11 soy beans, and others is first obtained in the manner well established in the art, which  
12 need not be described here. The vegetable flour, for example buckwheat flower, typically  
13 contains approximately 10 per cent (by weight) of protein and approximately 1 per cent  
14 (by weight) of phenolics. (All percentages in the present description are on a weight by  
15 weight basis, unless noted otherwise.)

16 In accordance with the process of the invention the vegetable flour is dissolved or  
17 suspended in a large excess of water, and while the solution or suspension is agitated  
18 alkali, such as sodium hydroxide or other nutritionally acceptable alkaline substance, is  
19 added until the pH of the solution/suspension is adjusted within the range of 8 to 13. A  
20 preferred pH range is 9.5 to 11.0. The alkaline solution/suspension is continuously  
21 agitated, preferably at an elevated temperature, such as in the range of 30 to 70 °C, for

1 sufficient time for the dissolved phenolics to undergo some oxidation to quinones and  
2 subsequent covalent attachment to the dissolved vegetable protein, probably by the  
3 chemical reactions described in the introductory section of this application for patent. In  
4 this connection again it is noted that whereas the above-described 1,4 (Michael) addition  
5 reaction is believed to be the predominant reaction by which the oxidized or partially  
6 oxidized phenolic compounds attach to the vegetable proteins under alkaline conditions,  
7 the present applicant does not wish to be bound by theory. Those skilled in the art will  
8 readily understand that the time required or utilized for the phenolics to undergo the  
9 above-described oxidation to quinones and covalent attachment depends on several  
10 factors, such as the temperature, the speed of agitation and the precise nature of the  
11 phenolics and of the protein. However, agitation under alkaline condition at an elevated  
12 temperature for a period of approximately 15 minutes to 2 hours is usually sufficient, a  
13 more preferred range of time is between 30 minutes to 1 hour.

14 In the next step of the process of the invention solids are removed from the  
15 alkaline solution/suspension by centrifugation or filtration. Generally speaking the  
16 removed solid materials comprise wet plant hulls, fibers and other insolubles and have no  
17 further significance or value from the stand-point of the present invention, and usually are  
18 discarded.

19 In the following step of the process, a nutritionally acceptable form of acid, such  
20 as hydrochloric acid is added to the liquid obtained previously by filtration or  
21 centrifugation until the pH is brought down into a range of approximately 2 to 7,

1 preferably into a range of 3.5 to 5.0. The liquid is preferably agitated while the acid is  
2 added, and preferably the mixture is allowed to warm spontaneously to, or if necessary is  
3 heated to an elevated temperature in the range of 30 to 70 °C. A presently preferred  
4 temperature both for the step of adjusting the pH to alkaline in the first step, and for  
5 acidifying the filtered solution in the present step is 55 °C. Nevertheless, those skilled in  
6 the art will understand that these process steps can be performed at ambient temperature  
7 as well. The acidified solution is allowed to agitate for a period of time, preferably in  
8 the range of 15 minutes to 2 hours , more preferably for 30 minutes to 1 hour, although  
9 the time is not critical. As a result of the acidification, vegetable protein and the  
10 vegetable protein bound phenolics precipitate out of the acidic solution, and are collected  
11 by filtration or centrifugation. After these solids are collected, the remaining liquid  
12 (supernatant) has no significance or value from the view point of the present invention,  
13 and can be utilized for other applications, or is discarded.

14 The collected solid material comprises vegetable protein bound phenolics and may  
15 also comprise vegetable protein molecules which have no phenolic moiety attached.  
16 Nevertheless, for the purpose of the present description the collected solid material is  
17 referred to as vegetable protein bound phenolics, with the understanding that, although  
18 this material is “rich” in phenolics, the bulk of its mass is composed of protein molecules,  
19 with the phenolics being randomly attached to the protein.

20 The collected solid is wet, and can subsequently be dried in processes and  
21 apparatus normally used in the food processing and related industry for this purpose.

1      Typically, the solids are dried in an atomizing spray drier, to yield a dry product rich in  
2      bound phenolics. The dry product obtained in this manner typically has an antioxidant  
3      capacity of 50 to 200 micromoles of trolox equivalent per mg. By comparison, soy  
4      protein isolate, containing 90% protein, 4% moisture, 4% ash, 1% fat, 1% carbohydrate,  
5      typically has an antioxidant capacity of 18 micromoles trolox equivalents per milligram.

6              This product, the vegetable protein bound phenolics, is then admixed with usual  
7      excipients known in the art to make tablets, capsules, soft-gel capsules or like delivery  
8      vehicles, in which the content of vegetable protein bound phenolics obtained above  
9      comprise approximately 25 to 95 weight percent of the tablet, capsule, soft-gel capsule or  
10     like delivery vehicle, and which typically have an antioxidant capacity of 10 to  
11     approximately 200 micromoles of trolox equivalent per mg of total material contained in  
12     the tablet, capsule, sof-gel capsule or like delivery vehicle. Stated in another way,  
13     typically each unit dose (tablet, capsule, soft gel capsule or the like) of the dietary  
14     supplement has an antioxidant capacity of 2500 to 200,000 micromoles of trolox  
15     equivalent per unit dose, and preferably approximately 20,000 to 100,000 micromoles of  
16     trolox equivalent per unit dose.

17              It should be understood in this connection that the excipient may or may not itself  
18      have nutritive value (for example it may include sugars and starch) , and that the tablets,  
19      capsule, soft-gel capsules or like delivery vehicles may contain additional vitamins,  
20      minerals or other known nutraceutical products. The term “excipient” as it is used in this  
21      description intends to cover all such ingredients which may be included in the tablets,

1 capsules, soft-gel capsules and the like that contain the vegetable protein bound phenolics  
2 in accordance with the invention.

3 Alternatively, the vegetable protein bound phenolics obtained above are  
4 incorporated in liquid or solid foods, such as shakes or bars, which typically have an  
5 antioxidant capacity of 500 to 20,000 micromoles of trolox equivalent per gram of the  
6 shake, bar or other food. The shakes, bars or other food products contain one or more  
7 conventional ingredients having nutritional and/or caloric value, such as sugars, syrups,  
8 chocolate, cocoa powder, natural or artificial flavors such as chocolate, vanilla or other  
9 flavors, lecithin, fats or oils (preferably vegetable oils) proteins from sources other than  
10 the vegetable protein bound phenolics of the invention. All the conventional nutritional  
11 products having caloric value and the flavor producing and other conventional ingredients  
12 are collectively termed “nutritional products” for the purposes of the present description.  
13 In addition to containing the vegetable protein bound phenolics and nutritional products,  
14 the shakes, bars or other food products of the invention may also contain vitamins,  
15 minerals or other known nutraceutical products.

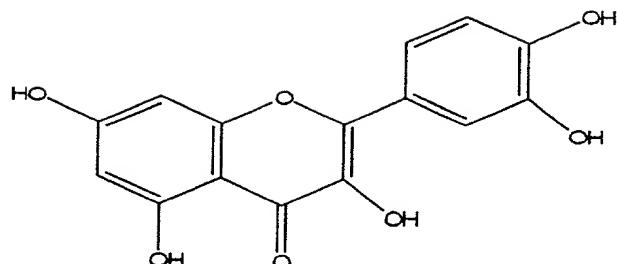
16 In accordance with another aspect of the present invention, additional phenolic  
17 material of the type which itself occurs naturally in many plants is added to the aqueous  
18 admixture of the vegetable flour before or while it is kept under alkaline condition.  
19 Exogenous phenolic materials which can be added to the vegetable protein in accordance  
20 with this aspect of the invention, include phenolic acids (caffeic acid, gallic acid),  
21 catechins (epicatechin, catechin, gallocatechin gallate, epigallocatechin gallate), flavones

1 (quercetin, myricetin, kaempferol), anthocyanidins (cyanidin, delphinidin, malvidin), or  
2 isoflavones (diadzein, genistein). The structure of quercetin is shown below. Generally  
3 speaking, 0.25 to 5 lbs of exogenous phenolic material (such as quercetin or any of the  
4 substances noted above, or combination of such phenolic substances) is added to 100 lbs  
5 of vegetable flour; the preferred range being 0.5 to 2.0 lbs of exogenous phenolics by 100  
6 lbs of vegetable flour, and a presently most preferred number is 1 lb of quercetin per 100  
7 lbs of vegetable flour.

8 The remaining steps of the process are then conducted as described above. In this  
9 manner, still higher concentrations of vegetable protein bound phenolics are contained in  
10 the final dried product, having an antioxidant capacity of 200 to 2000 micromoles of  
11 trolox equivalent per mg of the product. This product also, is made into tablets, capsules,  
12 soft-gel capsules or other delivery vehicles, or is incorporated into food products, such as  
13 shakes and bars. Depending on the amount of excipient used to make the tablets,  
14 capsules, soft-gel capsules or like delivery vehicles, these have an antioxidant capacity of  
15 50 to 2000 micromoles of trolox equivalent per mg of total material contained in the  
16 tablet, capsule, soft-gel capsule or like delivery vehicle (as above). Or stated in another  
17 way, each unit dose (tablet, capsule, soft-gel capsule or the like) has a an antioxidant  
18 capacity of 12,500 to 2,000,000 micromoles of trolox equivalent per unit dose and  
19 preferably 100,000 to 500,000 micromoles of trolox equivalent per unit dose.

20

21



8 Thus, in accordance with the present invention valuable foods, food or dietary  
9 supplements or nutraceuticals are obtained from materials which in the prior art were  
10 considered of little value. The present invention essentially counterdicts the teaching in  
11 the prior art which taught that it was necessary to remove phenolic materials from  
12 vegetable protein isolates.

13 **SPECIFIC EXAMPLES**

14 **Example 1: Buckwheat Phenol/Protein Isolation**

15 93 lbs. of buckwheat (*fagopyrum esculentum L.*) flour were added to 120 gallons  
16 of water. pH was adjusted to 10.05 by adding 2910 ml of 30% NaOH. Temperature was  
17 held at 55 °C under constant agitation for 30 minutes. The resultant mixture was pumped  
18 into a solids-ejecting disc centrifuge with a back pressure of 58 psi and a de-sludging  
19 cycle time of 3 minutes. The solids ejected by the centrifuge, consisting mostly of wet  
20 plant hulls, fiber and other insolubles, weighing 383 lbs. were discarded. The liquids  
21 were pumped through a 20 micron cartridge prefilter into a second tank. pH was adjusted

1 to 4.5 using 30% HCl to precipitate the phenol-protein complex. Temperature was kept  
2 at 55 °C for 30 minutes. The resultant mixture was pumped into a solids-ejecting disc  
3 centrifuge with a back pressure of 58 psi and a de-sludging cycle time of 4 minutes. The  
4 liquids that passed through the centrifuge (568 lbs.), consisting mostly of soluble  
5 carbohydrates and phenols not complexed to proteins, were kept for another application.

6 The solids ejected by the centrifuge (136.5 lbs.) consisting of the phenol/protein complex,  
7 were collected and fed into an atomizing spray drier of standard design using a Moyno  
8 pump at 1 gallon per minute flow rate. The product was sprayed from an atomizer with  
9 4mm orifices into a 7 foot-high tower. The spray-drier inlet temperature was 410 °F and  
10 the outlet temperature was 190 °F.

11 16 lbs. of dried product was obtained from the spray drier. The resultant product  
12 consisted of 64.3% protein, 4.0% moisture, 9.0% fat, 2.7% ash, and 20.0% carbohydrate.  
13 The product contained 0.4% free phenolic material. The product had an antioxidant  
14 capacity of 101 micromoles trolox equivalents per milligram. By comparison, soy protein  
15 isolate, containing 90% protein, 4% moisture, 4% ash, 1% fat, 1% carbohydrate, had an  
16 antioxidant capacity of 18 micromoles trolox equivalents per milligram.

17 Example 2. Introduction of Exogenous Phenols to a Buckwheat Phenol/Protein  
18 Isolation

19 100 lbs. of buckwheat (*fagopyrum esculentum L.*) flour and 1 lb. of quercetin  
20 were added to 100 gallons of water. pH was adjusted to 11.02 by adding 30% KOH.  
21 Temperature was held at 55 °C under constant agitation for 45 minutes. The resultant

1 mixture was pumped into the same solids-ejecting disc centrifuge as described in  
2 Example 1. The solids ejected by the centrifuge, consisting mostly of wet plant hulls,  
3 fiber and other insolubles, were discarded. The liquids were pumped through a 20  
4 micron cartridge prefilter into a second tank. pH was adjusted to 4.03 using 30% HCl to  
5 precipitate the phenol-protein complex. Temperature was kept at 55 °C for 30 minutes.  
6 The resultant mixture was pumped into a solids-ejecting disc centrifuge. The liquids that  
7 passed through the centrifuge (472 lbs.), consisting mostly of soluble carbohydrates and  
8 phenols not complexed to proteins, were kept for another application. The solids ejected  
9 by the centrifuge (218 lbs.) consisting of the phenol/protein complex, were collected and  
10 fed into an atomizing spray drier of standard design using a Moyno pump at 1 gallon per  
11 minute flow rate. The product was sprayed from an atomizer with 4mm orifices into a 7  
12 foot-high tower. The spray-drier inlet temperature was 410 °F and the outlet temperature  
13 was 190 °F. 16 lbs. of product was obtained from the spray drier. The resultant product  
14 consisted of 63.9% protein, 4.1% moisture, 10.0% fat, 2.6% ash, and 19.4%  
15 carbohydrate. The product had an antioxidant capacity of 834 micromoles trolox  
16 equivalents per milligram.

17 Example 3. Introduction of Exogenous Phenols to a Hops Phenol/Protein Isolation

18 100 lbs. of defatted hops (*humulus lupulus L.*) flour and 1 lb. of quercetin were  
19 added to 100 gallons of water. pH was adjusted to 10.05 by adding 30% KOH.  
20 Temperature was held at 55 °C under constant agitation for 45 minutes. The resultant  
21 mixture was pumped into the same solids-ejecting disc centrifuge as described in

1 Example 1. The solids ejected by the centrifuge, consisting mostly of wet plant hulls,  
2 fiber and other insolubles, were discarded. The liquids were pumped through a 20  
3 micron cartridge prefilter into a second tank. pH was adjusted to 4.48 using 30% HCl to  
4 precipitate the phenol-protein complex. Temperature was kept at 55 °C for 30 minutes.  
5 The resultant mixture was pumped into a solids-ejecting disc centrifuge. The liquids that  
6 passed through the centrifuge (528 lbs.) consisting of soluble carbohydrates, soluble  
7 proteins, and soluble phenols not bound to insoluble protein, were retained for another  
8 application . The solids ejected by the centrifuge (139 lbs.) consisting of the  
9 phenol/protein complex, were collected and fed into an atomizing spray drier of standard  
10 design using a Moyno pump at 1 gallon per minute flow rate. The product was sprayed  
11 from an atomizer with 4mm orifices into a 7 foot-high tower. The spray-drier inlet  
12 temperature was 410 °F and the outlet temperature was 190 °F.  
13

14 11 lbs. of product was obtained from the spray drier. The resultant product  
15 consisted of 71.2% protein, 3.9% moisture, 8.8% fat, 3.0% ash, and 13.1% carbohydrate.  
16 The product had an antioxidant capacity of 590 micromoles trolox equivalents per  
17 milligram.

18 Example 4. Shake

19 3 lbs. of the phenolated buckwheat protein of Example 2 was mixed with 6 lbs. of  
20 soy protein isolate, 13 lbs. of crystalline fructose, 5 lbs. of Dutch processed cocoa, 0.2  
21 lbs. stevia extract, 0.1 lbs. lecithin, 0.05 lbs. medium chain triglycerides, 0.09 lbs.  
ascorbic acid, 0.03 lbs. vitamin E acetate, 0.02 lbs. digestive enzyme mix (Aminogen™).

- 1 This made 150 30 gram packets. The packets were mixed with 8 oz. of skim milk to
- 2 make a protein shake for use as a snack, exercise supplement, or meal replacement.

1      Example 5. Bar

2            The following Table provides the ingredients for an exemplary bar incorporating  
3            the phenolated protein of Example 3.

4	Number	Ingredient	Weight
			%
5	1	Maltitol Syrup	6.410
6	2	Cocoa Powder	4.487
7	3	Chocolate Chips	3.846
8	4	Glycerine	15.385
9	5	Natural Flavors	1.923
10	6	Potassium Sorbate	0.256
11	7	Dicalcium Phosphate	0.962
12	8	Magnesium Oxide	0.064
13	9	Vitamin A Palmitate	0.060
14	10	Ascorbic Acid	0.045
15	11	Vitamin E Acetate	0.015
16	12	Niacinamide	0.010
17	13	Ferrous Fumarate	0.010
18	14	Zinc Oxide	0.010
19	15	Pantothenic Acid	0.005
20	16	Pyridoxine HCl	0.001
21	17	Copper Gluconate	0.001
22	18	Cholecalciferol	0.0007
23	19	Riboflavin	0.0007
24	20	Thiamine Mononitrate	0.0007
25	21	Folic Acid	0.0001
26	22	Biotin	0.00005
27	23	Potassium Iodide	0.0001
28	24	Cyanocobalamin	0.00001
29	25	Soy Protein Isolate	28.205
30	26	Phenolated Hops	12.821
		Protein	
31	27	Maltitol Syrup	12.821
32	28	Fractionated Vegetable Oils	5.128
33	29	Cocoa	3.846
34	30	Calcium Caseinate	2.564
35	31	Lecithin	0.641
36	32	Vanilla	0.513
37	33	Sucralose	0.128

38

1           The composition was prepared by combining items 1, 2, and 3 from the above  
2       Table, and heating to 245 ° F., followed by transfer to a mixer. To the heated  
3       composition were added items 4, 5 and 6 of the Table and the mixture was agitated for  
4       over 2 minutes. The mixture was cooled to 140 ° F. and item 6 was added and mixed for 1  
5       minute. To the mixture was then added a pre-blend of items 7-24 of the Table, followed  
6       by mixing for 2 minutes. Items 25 and 26 were then added and the resulting mixture  
7       agitated for 2 minutes. The mixture was allowed to cool and cut into rectangles or bars  
8       with each bar weighing approximately 60 grams. To each bar was added a coating  
9       consisting of a hot mixture (140 ° F) of items 27 to 33 of the Table. Finally items 17-21  
10      of the Table were added and the mixture agitated for 4 minutes. The resultant bars  
11      weighed approximately 80 grams and each contained approximately 10 grams of the  
12      phenolated hops protein of Example 3.

13      **Example 6. Capsule**

14           3 lbs. of the phenolated buckwheat protein of Example 2 was placed into size “0”  
15       hard-shell gelatin capsules in a capsule filling machine. 400 mg of phenolated buckwheat  
16       protein was filled into each capsule. 3400 capsules were obtained.

17      **Example 7. Tablet**

18           3 lbs. of the phenolated buckwheat protein of Example 2 was mixed with 1 lb. of  
19       calcium diphosphate and 0.1 lb. of magnesium stearate and placed in a Glatt fluid-bed

1 granulator. The resultant agglomerated powder was introduced to a tablet press. 525 mg  
2 of the mixture was pressed into each tablet, representing 400 mg of phenolated  
3 buckwheat protein. 3100 tablets were obtained.

4